time the concentration of the solution will become variable in direct proportion to its dilution, or we can state conversely that at constant temperature, the changing of the acid concentration in proportion to the dilution is indicative of one and only one solid phase—one chemical individual.

(3) The two highest chromates of mercury, lead and bismuth, are respectively $HgCr_2O_7$, $HgCrO_4$, $PbCr_2O_7$, $PbCrO_4$, $Bi_2O_3.4CrO_3$ and $Bi_2O_3.2CrO_3$.

(4) In accord with the phase rule each of these salts has a certain hydrolytic dissociation pressure, *i. e.*, a certain minimum acid concentration below which it is not stable. Without a knowledge of these concentrations it is not, in general, possible to prepare the salts pure.

The hydrolytic dissociation pressures for the above salts in gram-molecules of CrO_3 per liter at 25° are:

1.	$HgCr_2O_7$	10.46
	$HgCrO_4$	0.46
2.	$PbCr_2O_7$	6.87
	$PbCrO_4$	0.00002
3.	$Bi_2O_3.4CrO_3$	7.80
	$Bi_2O_3.2CrO_3$	0.00001

All of these salts require an acid of the above concentration as a minimum for their formation and to maintain their stability.

(5) The existence in the pure form of the second highest chromates is limited by a maximum acid concentration equal to the minimum concentration of the next higher chromate, while the existence of the highest chromates is limited only by their own solubility and that of chromium trioxide. This is easily seen from the figures in the text.

LELAND STANFORD, JR., UNIVERSITY, CALIF.,
March, 1906.

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY.]

THE CHANGE FROM GREEN TO VIOLET IN CHROMIUM CHLORIDE SOLUTION.

BY ARTHUR B. LAMB.

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Weinland and Koch[1] have recently disclosed some interesting facts regarding the precipitability of the chlorine in the green

[1] Weinland and Koch: Z. anorg. Chem. 39, 256 (1904).

hydrate of chromic chloride, $CrCl_36H_2O$, by silver salts. Working first *without* the addition of acid they found that while silver salts of strong acids do *not* produce complete precipitation, even when present in great excess, silver salts of very weak acids, added in equivalent amounts, produce immediate and complete precipitation. They are at a loss to explain this unusual phenomenon, and point out that this is the first instance known, where, the *anion* influences the reactions of its cation. In what follows, I think there will be found a plausible explanation of this unexpected behavior.

Godefroy[1] and Recoura[2] early observed that hydrochloric acid, when added to solutions of the green chloride of chromium, retards the change to the violet modification. Weinland and Koch,[3] in studying the precipitability of the green chloride in *acid* solution, obtained results agreeing with this observation. They found that strong acids, such as nitric, chloric, perchloric and permanganic, can prevent the precipitation of two of the three chlorine atoms; sulphuric and lactic acids can hinder the precipitation to a somewhat less extent, while acetic acid can only prevent the precipitation of a single atom of chlorine. Evidently then, the stronger the acid, or in other words, the greater the concentration of the hydrogen ion, the less the precipitation. Now the increasing precipitability of the green salt is undoubtedly due to its gradual reversion to the completely precipitable violet modification. Whatever, then, hinders this change is unfavorable to complete precipitation. That hydrogen ions do lessen the precipitability is therefore in precise accordance with the observation of Godefroy and Recoura.

I have tested the effect of hydrogen ions on the rate of change of the green into the violet modification in a somewhat more exact manner, by following the change in the electrical conductivity of the solutions, Werner and Gubser[4] having shown that the green and the violet modifications have very different molecular conductivities.

Curve I shows the rate of change of the conductivity with the time when the solution contained nothing but the chromic chlo-

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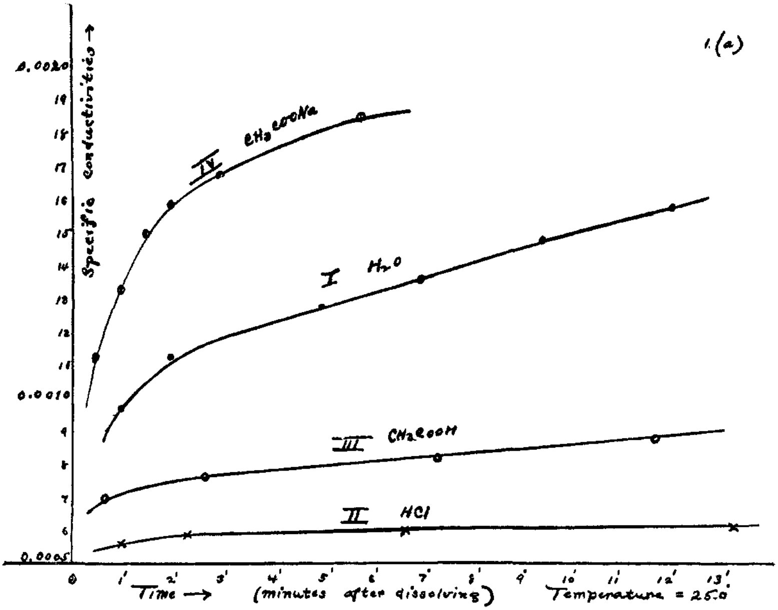
[1] Godefroy: Compt. rend. 100, 105 (1885).

[2] Recoura: Ann. chim. phys. [6] 10, 37 (1887).

[3] Weinland and Koch: Loc. cit.

[4] Werner and Gubser: Ber. 34, 1597 (1901).

ride. Curve II shows the change when an approximately equivalent amount of hydrochloric acid was present. Curve III shows the same thing when a considerable excess (20 times) of acetic acid was present.[1]



It is seen that a marked paralysis of the change is produced by the addition of the strong acid and a much slighter one by the addition of the weak acid. I now dissolved the chloride in an approximately equivalent solution of sodium acetate. In this solution the concentration of the hydrogen ion must have been

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[1] The solutions were all N/125 as regards chromic chloride. The hydrochloric acid and the acetic acid solutions were N/125 and N/6, respectively, as regards the acids themselves.

The specific conductivities represent the differences between the specific conductivities of the solution before and after the addition of the chromic chloride.

The addition of the sodium acetate not only accelerated the change but altered the location of the equilibrium. The specific conductivity never got much beyond 0.00200; that is, the final equilibrium was reached in an hour, while in pure water equilibrium is only reached after a day or more.

It is entirely an open question whether the conductivity is a linear function of the concentrations of the two kinds of chromium. This question does not, however, affect a *comparison* such as is here made.

even smaller than in pure water, because of the relatively high concentration of the action. The change ought here then to be *more rapid* than in pure water. Curve IV shows that this was indeed the case.

From these experiments, the observation of Godefroy and Recoura and the experiments of Weinland and Koch in acid solution, it seems reasonable to conclude that the concentration of the hydrogen ion has a marked influence on the rate of the color change, but what is still more convincing is that the previously inexplicable variable precipitating power of the different silver salts in neutral solution as observed by Weinland and Koch and referred to above is easily explicable on this basis.

Chromic chloride solutions of themselves contain a definite concentration of hydrogen ions, depending on the concentration of the solution and the temperature; that is, they are hydrolyzed. When a silver salt is added to such a solution an equilibrium must be established between the hydrogen ions in solution and the anions of the added salt. The location of this equilibrium is determined, since other factors are constant, by the dissociation constant of the acid from which the silver salt is derived. The weaker the acid the less the concentration of hydrogen ion compatible with a given concentration of the anion, and the concentration of the anion is relatively large. It follows that the weaker the acid from which the added silver salt is derived, the less will the transformation into the violet modification be retarded and hence the *greater will be the amount of chlorine precipitated.* This is, as we have seen, precisely what Weinland and Koch found to be the case.

The only explanation which I have as yet been able to frame for this striking action of the hydrogen ion, is that one step in the process of isomerization is the formation of a *hydrolyzed derivative* of *chromic chloride.* Now in the case of a salt like chromic chloride there are two possible sorts of hydrolysis, due to the fact that there are two sorts of chlorine atoms present, the precipitable and the non-precipitable.

The first sort of hydrolysis would be of the usual electrolytic type. The complex cation would unite with the hydroxyl ion to form the undissociated base.

$$(CrCl_2)^{\cdot} + Cl' + OH' + H \rightleftarrows (CrCl_2)OH + Cl' + \dot{H}.$$

At equilibrium the concentration of the base would evidently be directly proportional to the concentration of the hydroxyl ion and hence through the equilibrium with water of constant concentration inversely proportional to the concentration of the hydrogen ion. If this hydrolyzed derivative were the compound which actually changed over to the violet modification, and if this change were the slow step in the whole process, then the velocity of the color change as a whole would be proportional to the concentration of the hydroxyl ion and therefore inversely proportional to the concentration of the hydrogen ion. This then would explain the observed retarding effect of hydrogen ions on the color change and on precipitation.

The same can be said of the second sort of hydrolysis. Here the hydroxyl ion, always present in aqueous solution, substitutes for both chlorine atoms in the *complex*, the chlorine ion requiring the negative charge of the hydroxyl ion. We may either consider that this in itself destroys the green complex, or what amounts to practically the same thing, that the green instantly changes to the violet modification, with accompanying instantaneous dissociation of the hydroxyl ions. The formation of the hydroxyl compound would then be the slow step in the whole process of isomerization, and since its velocity would be directly proportional to the concentration of the hydroxyl ions (or to the square of their concentration) and therefore inversely proportional to the concentration of the hydrogen ions, the velocity of the whole process would itself be inversely proportional to the concentration of the hydrogen ion. Both sorts of hydrolysis then would give results in accordance with the observations.

Both sorts of hydrolysis undoubtedly take place in aqueous solutions of chromic chloride. But there are reasons for believing that the latter sort of hydrolysis probably constitutes the essential, efficient step in the transformation of the green modification into the violet. Thus Pfeiffer[1] found that with certain pyridine derivatives of the hexahydrates of chromic chloride and bromide, when treated with pyridine or ammonia, yielded a precipitate of hydroxy-chloride or -bromide, and that this precipitate, if allowed to remain in contact with the precipitant, changed its color, and when redissolved in acids gave violet solutions. Acids and alkalies have a similar effect on the interconversion of the roseo and

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[1] Pfeiffer: Ber. 39, 1879 (1906).

purpureo ammonio salts of chromium. Recoura,[1] long ago, observed a similar behavior when ordinary green chromic chloride was treated with alkalies. Furthermore, Pfeiffer[2] found that a yellowish green isomer of the above pyridine derivatives was similarly changed into the violet modification by the action of pyridine or ammonia, although none of its chlorine was precipitable with silver nitrate, which in this case, at least, precludes the first sort of hydrolysis.

From this point of view, the color change in pure aqueous solutions of green chromic chloride would become a rather interesting type of reaction. The hydrolysis of the chlorine ions in the green complex would be taking place in a solution whose hydroxyl ion concentration, and consequently whose hydrogen ion concentration, would be governed by the degree of hydrolysis of the green complex ion, ($CrCl_2'$) disappearing, and of the violet ion (Cr''') being formed. If the latter were less hydrolyzed than the former, the hydrogen ion concentration would *decrease* as the color change progressed, and we should have a case of auto-catalysis. If, on the other hand, the latter were more hydrolyzed, the concentration of the hydrogen ion would *increase* and we should have a case of *negative* auto-catalysis.

This color change in solutions of chromic salts is being further investigated experimentally in this laboratory, particularly as regards its velocity and the location of its equilibrium.

THE TECHNICAL ESTIMATION OF ANTIMONY AND ARSENIC IN ORES, ETC.

By A. H. Low.

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The technical estimation of antimony in ores containing also arsenic and possibly tin is frequently a tedious and more or less unsatisfactory operation. Distillation methods may give correct results, but considerable experience in their manipulation is usually required, and perhaps, also, special apparatus not always at the disposal of the technical chemist having only an occasional antimony determination to make. The following method for both antimony and arsenic is free from these objections, and,

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[1] Recoura: Loc. cit.

[2] Pfeiffer: Loc. cit.